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Chemical reaction rate determination I. numerical differential methods

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Summary. Chemical reaction rates are determined mainly by linear plots of reagent concentration terms or its logarithm (depending on the order) against time with initial concentration -equivalent to the final property reading at infinite time- specified, which can be experimentally challenging. By definition, the rate constant is an invariant quantity and the kinetic equations follow this assumption. Different schemes have been used to circumvent specifying initial concentrations. In this sequel, the differential method using nonlinear analysis (NLA)focuses on the gradient which provides a sensitive measure of the rate constant that does not require specification of initial concentrations and the results are compared with those derived from standard methodologies from an actual chemical reaction and one simulated ideally. It is shown that the method is feasible. A novel integral approach based on a principle of induced parameter dependence (PIPD) is introduced in the second sequel. It is concluded that elementary nonlinear methods in conjunction with experiments could play a crucial role in providing accurate values of various parameters of interest.

1 INTRODUCTION

The gradient methods are tested against a first order chemical reaction (reaction (i))whereas the PIPD application in the second sequel is tested against the same first order reaction and a second order reaction (reaction (ii)) The details are
(i) the first-order reaction involving the methanolysis of ionized phenyl salicylate with data derived from the literature [1, Table 7.1,p.381] with presumably accurate values of both the initial concentration and all other data sets of the kinetic run and
(ii) the reaction between plutonium(VI) and iron(II) according to the data in [2, Table II p.1427] and [3, Table 2-4, p.25].

Reaction (i) may be written

$$PS^- + CH_3OH \xrightarrow{k_a} MS^- + PhOH \qquad (1)$$

where for the rate law is pseudo first-order expressed as

$$\text{rate} = k_b[\text{PS}]^- = k_c[\text{CH}_3\text{OH}][\text{PS}^-].$$

The methanol concentration is in excess and is effectively constant for the reaction runs [1, p.407]. The data for this reaction is given in detail in [1, Table 7.1], conducted at 30°C where several ionic species are present in the reaction solution from KOH, KCl, and H_2O electrolytes.

2 First-Order Gradient results

The change in time t for any material property $\lambda(t)$, which in this case is the Absorbance $A(t)$ (i.e. $A(t) \equiv \lambda(t)$is given by

$$\lambda(t) = \lambda_\infty - (\lambda_\infty - \lambda_0)\exp(-k_a t) \tag{2}$$

for a first order reaction where λ_0 refers to the measurable property value at time $t = 0$ and λ_∞ is the value at $t = \infty$ which is usually treated as a parameter to yield the best least squares fit in the conventional analysis.The method presented here is *not* confined to first order reactions; it applies to any order provided the expressions can be expanded as an n-order polynomial of the concentration variable against the time independent variable.

2.1 Orthogonal polynomial stabilization

It was discovered that the usual least squares polynomial method using Gaussian elimination [4, Sec.6.2.4,p.318]to derive the coefficients of the polynomial was highly unstable for $npoly > 4$, which is a known condition [4, p.318,Sec 6.2.4]where for higher orders, there exists the tendency to form kinks and loops for values between two known intervals. The usual method defines the n^{th} order polynomial $p_n(t)$ which is then expressed as a sum of square terms over the domain of measurement to yield Q in (3).

$$\begin{aligned} p_n(t) &= \textstyle\sum_{j=0}^{n} h_j t^j \\ Q(f, p_n) &= \textstyle\sum_{i=1}^{N} [f_i - p_n(t_i)]^2 \end{aligned} \tag{3}$$

The Q function is minimized over the polynomial coefficient space. In the Orthogonal polynomial (OP) method, we express our polynomial expression $p_m(t)$ linearly in coefficients a_j of φ_j functions that are orthogonal with respect to an *inner* product definition. For arbitrary functions f, g, the inner product (f, g) is defined below, together with properties of the φ_j orthogonal polynomials.

$$\begin{aligned} (f,g) &= \textstyle\sum_{k=1}^{N} f(t_k).g(t_k) \\ (\varphi_i, \varphi_j) = 0 \ (i \neq j);& \text{ and } (\varphi_i, \varphi_i) \neq 0. \end{aligned} \tag{4}$$

$$\begin{aligned} \varphi_i(t) &= (t - b_i)\varphi_{i-1}(t) - c_i\varphi_{i-2}(t)\,(i \geq 1) \\ \varphi_0(t) &= 1, \text{and } \varphi_j = 0 \ \ j < 1, \\ b_i &= (t\varphi_{i-1}, \varphi_{i-1})/(\varphi_{i-1}, \varphi_{i-1})\ (i \geq 1), 0\,(i < 1) \\ c_i &= (t\varphi_{i-1}, \varphi_{i-2})/(\varphi_{i-2}, \varphi_{i-2})\ (i \geq 2), 0\,(i < 2). \end{aligned} \tag{5}$$

We define the m^{th} order polynomial and associated a_j coefficients as:

$$\begin{aligned} p_m(t) &= \textstyle\sum_{j=0}^{m} a_j \varphi_j(t) \\ a_j &= (f, \varphi_j)/(\varphi_j, \varphi_j), (j = 0, 1, \ldots m) \end{aligned} \tag{6}$$

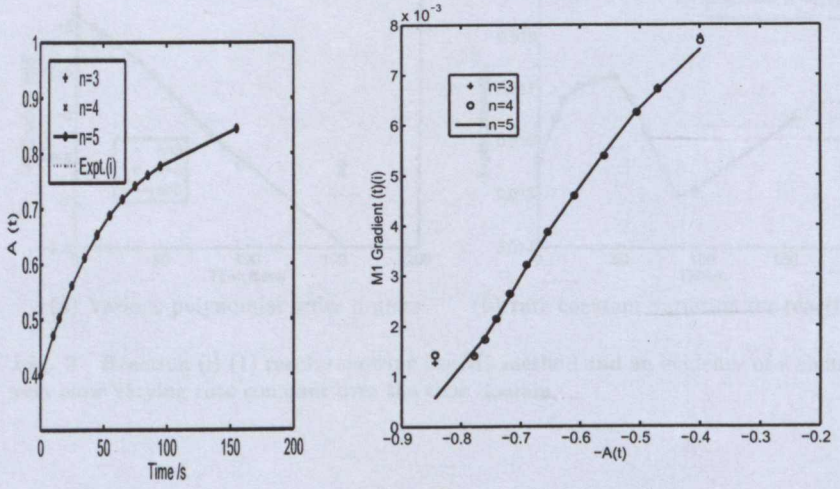
The recursive definitions for the first and second derivatives are given respectively as:

$$\begin{aligned} \varphi_i'(t) &= \varphi_{i-1}'(t)(t-b_i) + \varphi_{i-1}(t) - c_i\varphi_{i-2}'(t)\,(i \geq 1) \\ \varphi_i''(t) &= \varphi_{i-1}''(t)(t-b_i) + 2\varphi_{i-1}'(t) - c_i\varphi_{i-2}''(t)\,(i \geq 2) \end{aligned} \tag{7}$$

Here the codes were developed in C/C++ which provides for recursive functions which we exploited for the evaluation of all the terms. The experimental data were fitted to an m^{th} order expression $\lambda_m(t)$ defined below

$$\lambda_m(t) = \sum_{j=0}^{n} h_j t^j \tag{8}$$

The coefficients h_i are all computed recursively, and the derivatives determined from (8) or from (6) and (7). The orthogonal polynomial method is very stable but the curvature of these polynomial expressions will increase with increasing n, giving a poorer value of k, whereas higher values of n would better fit the $\lambda\, vs\, t$ curve. Hence inspection of the plots is necessary to decide on the appropriate n value, where we choose the lowest n value for the most linear graph of the expression under consideration that also provides a good $\lambda(t)$ fit over a suitable time range over which the k rate constants apply. There is in practice little ambiguity in selecting the appropriate polynomials, as will be demonstrated. Fig.(1(a)) illustrates the



(a) Experimental and fitted values.

(b) M1 results.

Fig. 1 Reaction (i) (1) results.

close fit between the experiment and the OP method that cannot be achieved with the least squares method without stabilization. We also quote some values of Khan's results [1, Table 7.1] in Table (1) for reaction (i), (1). 1(b)

2.2 Method 1

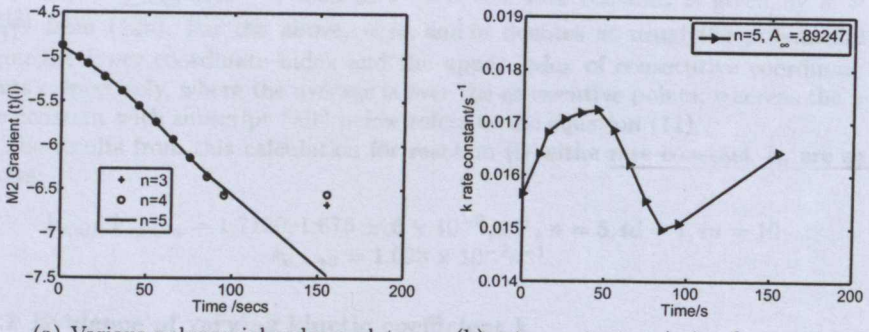
This method (M1) states that for constant k, the rate equation $\frac{dc}{dt} = -kc = -k(a-x)$ reduces for oru example reaction to

$$\frac{\lambda(t)}{dt} = -k_a\lambda(t) + \lambda_\infty . k_a \tag{9}$$

$10^3 \sum d_i^2$	513.5	109.4	8.563	63.26	212.7	227.4
A_∞	.8805	.881	.882	.883	.885	.887
$10^3 k/s^{-1}$	$19.7 \pm .6$	$18.1 \pm .3$	$16.5 \pm .1$	$15.5 \pm .2$	$14.2 \pm .4$	$13.3 \pm .5$

Table 1 Some results from reaction (i) (1) [1, p.381,Table 7.1].The first row refers to the square difference summed, where the lowest value would in principle refer to the most accurate value (third entry from left). The second row refers to the A_∞ absorbance and the last to the corresponding rate constant with the most accurate believed at the stated units to be at $16.5 \pm .1$.

Hence a plot of $\frac{\lambda(t)}{dt}$ vs $\lambda(t)$ would be linear. The results for reaction (i) are graphed in Fig.(1(b)) where we find that the gradients were smooth for the first 10 or so points and reasonably linear, but that at the boundary of these selected points, there are deflections in the curve; on the other hand , the different order polynomial curves ($n \leq 5$) are all coincident over a significant range of these values; we chose the $n = 5$ polynomial curve to determine the curve over the entire range and the linear least squares fit yields the following data $k_b = 1.64 \pm .04 \times 10^{-2} \mathrm{s}^{-1}$ and $A_\infty = 0.8787 \pm .0008$ units which should be compared to Khan's results in Table(1). The agreement is very close.



(a) Various polynomial order n plots. (b) rate constant variation for reaction (i).

Fig. 2 Reaction (i) (1) results showing the M2 method and an evidence of a sinusoidally very slow varying rate constant over the time domain.

2.3 Method 2

For reaction (i) Let $\alpha' = \lambda_\infty - \lambda_0$, then $\ln \alpha' - \ln(\lambda_\infty - \lambda) = kt$, then noting this and differentiating yields

$$\underbrace{\ln\left(\frac{d\lambda}{dt}\right)}_{Y} = \underbrace{-kt}_{Mt} + \underbrace{\ln[k(\lambda_\infty - \lambda_0)]}_{C} \tag{10}$$

A typical plot that can extract k_a as a linear plot of $\ln(d\lambda/dt)$ vs t is given in Fig.(2(a)) for Method 2, reaction (i)where the analysis uses $npoly = 5$. The linear least square line yields for Method 2 the following:

$$k_a = 1.72 \pm .02 \times 10^{-2} \mathrm{s}^{-1} \text{ and } A_\infty = 0.86(53) \pm .02 \text{ units.}$$

We note that because of the manifest nonlinearly of the gradients, one cannot determine the A_∞ values to 4-decimal place accuracy as quoted by Khan based on his

model and assumptions [1, Table 7.1]. However, we conclude that Method 1 which does not take logarithms is a much more accurate method.

2.3.1 Method 1 variation

A variant method similar to the Guggenheim method [5] of elimination is given below but where gradients to the conductivity curve is required, and where the average over all pairs is required; the equation follows from (10).

$$\langle k \rangle = \frac{-2}{N(N-1)} \sum_{i}^{N} \sum_{j>i}^{N} \ln \left(\lambda'(t_i)/\lambda'(t_j) \right) / (t_i - t_j) \tag{11}$$

Since we are averaging over instantaneous k values, there would be a noticeable standard deviation in the results if the hypothesis of change of rate constant with species concentration is correct. Differentiating (10) for constant k leads to (12) expressed in two ways

$$\frac{d^2\lambda}{dt^2} = -k \left(\frac{d\lambda}{dt} \right) (a) \text{ or } k = -\frac{d^2\lambda}{dt^2} / \left(\frac{d\lambda}{dt} \right) (b) \tag{12}$$

If $\lambda(t) = \sum_{i=0}^{n+1} a(i) t^{i-1}$, then as $t \to 0$, the rate constant is given by $k = \frac{-2a(2)}{a(1)}$ from (12b). For the above, $n, id,$ and iu denotes as usual the polynomial degree,the lower coordinate index and the upper index of consecutive coordinate points respectively, where the average is over the consecutive points, whereas the k rate constant with subscript "all" below refers to the equation (11) .

The results from this calculation for reaction (i) withe rate constant k_a are as follows:

$$k_{a,all}, k_{a,id,iu} = 1.7150, 1.676 \pm .3 \times 10^{-2}, \mathrm{s}^{-1},\ n = 5, id = 1, iu = 10$$
$$k_{a,t\to 0} = 1.023 \times 10^{-2} \mathrm{s}^{-1}.$$

2.3.2 Evidence of varying kinetic coefficient k

Under the linearity assumption $x = \alpha\lambda(t)$, the rate law has the form $dc/dt = -k(t)(a - x)$ where $k(t)$ is the instantaneous rate constant and this form implies

$$k(t) = \frac{d\lambda/dt}{(\lambda_\infty - \lambda(t))} \tag{13}$$

If λ_∞ is known from accurate experiments or from our computed estimates, then $k(t)$ is determined; the variation of $k(t)$ could provide crucial information concerning reaction kinetic mechanism and energetics, from at least one theory recently developed for elementary reactions [6] *at equilibrium*; the results for reaction (i) based on our data is shown in Fig.(2(b)). Barring experimental systematic errors and artifacts, the result is consonant with two separate effects: (α) a long-time limit due to changes in concentration that alters the force fields and consequently the mean rate constant value (according to the theories in [6, 7]) of the reaction as equilibrium is reached, and (β) possible transient effects due to collective modes of the coupling between the reacting molecules and the bulk solution as observed in the region between the start of the reaction and the long-time interval.

2.3.3 Optimization of first and second derivative expressions

Differentiating (10) for constant k leads to (12) expressed in two ways

$$\frac{d^2\lambda}{dt^2} = -k\left(\frac{d\lambda}{dt}\right)(a) \text{ or } k = -\frac{d^2\lambda}{dt^2}/\left(\frac{d\lambda}{dt}\right)(b) \tag{14}$$

Define $\frac{d\lambda}{dt} \equiv dl$ and $\frac{d^2\lambda}{dt^2} \equiv d2l$. Then $dl(t) = A\exp(-kt)$ and $dl(0) = A = h_2$ from (8).Furthermore, as $t \to 0$, $k = (-2h_2/h_1)$ and a global definition of the rate constant becomes possible based on the total system $\lambda(t)$ curve.

With a slight change of notation, we now define dl and $d2l$ as referring to the continuous functions $dl(t) = A\exp(-kt)$ and $d2l(t) = -kA\exp(-kt)$ and we consider $(d\lambda/dt)$ and $d^2\lambda/dt^2$ to belong to the values (8) derived from ls fitting where $(d\lambda/dt) = \lambda'_m$, $(d^2\lambda/dt^2) = \lambda''_m$ which are the experimental values for a curve fit of order m. From the experimentally derived gradients and differentials, we can define two non-negative functions $R_\alpha(k)$ and $R_\beta(k)$ as below:

$$\begin{aligned} R_\alpha(k) = &\quad \textstyle\sum_{i=1}^{N}\left(\frac{d^2\lambda(t_i)}{dt^2} + kdl(t_i)\right)^2 \\ R_\beta(k) = &\quad \textstyle\sum_{i=1}^{N}\left(\frac{d\lambda(t_i)}{dt} - dl(t_i)\right)^2 \\ &\text{where} \\ f_\alpha(k) = R'_\alpha(k) &\text{ and } \quad f_\beta(k) = R'_\beta(k) \end{aligned} \tag{15}$$

and a stationary point (minimum) exists at $f_\alpha(k) = f_\beta(k) = 0$. We solve the equations f_α , f_β for their roots in k using the Newton-Raphson method to compute the roots as the rate constants k_α and k_β for functions $f_\alpha(k)$ and $f_\beta(k)$ respectively. The error threshold in the Newton-Raphson method was set at $\epsilon = 1.0 \times 10^{-7}$ We provide a series of data of the form $[n, A, k_\alpha, k_\beta, \lambda_{\alpha,\infty}, \lambda_{\beta,\infty}]$ where n refers to the polynomial degree, A the initial value constant as above, k_α and k_β are the rate constants for the functions f_α and f_β (solved when the functions are zero respectively) and likewise for $\lambda_{\alpha,\infty}$ and $\lambda_{\beta,\infty}$. The λ_∞ values are averaged over the stated data points from the equation

$$\lambda_\infty = \frac{d\lambda(t)}{dt}\frac{1}{k} + \lambda(t) \tag{16}$$

for scheme α and β for reaction (i). The results for this system are
$[5, 7.5045 \times 10^{-3}, 1.2855 \times 10^{-2}, 1.5497 \times 10^{-2}, .94352, .89247]$
for the first 12 datapoints of the published data to time coordinate 155secs and polynomial order $n = 5$. For polynomial order 2, 4 and the first 11 datapoints, where there are no singularities in the curve we have
$[3, 7.7275 \times 10^{-3}, 1.4469 \times 10^{-2}, 1.6147 \times 10^{-2}, .91320, .88335]$
$[4, 7.4989 \times 10^{-3}, 1.3146 \times 10^{-2}, 1.5359 \times 10^{-2}, .94208, .89652]$.
Here, k_α and k_β differ by $\sim .2 \times 10^2 s^{-1}$; one possible reason for this discrepancy is the insufficient number of datapoints to to accurately determine $\frac{d^2\lambda}{dt^2}$. Hence experimentalists who wish to employ NLA must provide more experimental points, especially at the linear region of the $\lambda(t)\, vs\, t$ curve. Again for method β, the calculated values are close to the experimentally derived values of Khan.

3 Inverse Calculation

Rarely are experimental curves compared with the ones that must obtain from the kinetic calculations. Since the kinetic data is the ultimate basis for deciding on values

Result	Procedure	Poly. order	λ_∞	k_a
1	From expt	-	.8820	1.65×10^{-2}
2	Method 1	5	.8787	1.64×10^{-2}
3	Method 2	5	.8653	1.72×10^{-2}
4	sec(2.3.3) R_β	5	.89247	1.5497×10^{-2}

Table 2 Data for the plot of Fig.(3) for reaction (i).

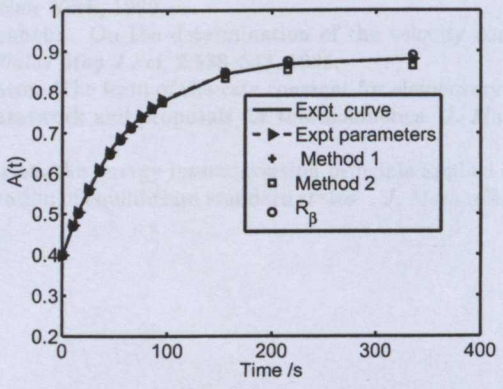


Fig. 3 The plots according to the k_b and A_∞ values of Table(2)

of the kinetic parameters, re plotting the curves with the calculated parameters to obtain the most fitting curve to experiment would serve as one method to determine the best method amongst several. For reaction (i) we have the following data:

Fig.(3) indicate that for reaction (i), we note a good fit for all the curves, that of the experiment, Khan's results and ours.

4 Conclusions

The results show that the use of differential NLA allows one to probe into the finer details of kinetic phenomena that the standard integral techniques are not equipped to handle especially where changes of rate constant is implicated during the course of the reaction. Even if the assumption of k invariance is made, the best polynomial choice can be determined by inspection, and the rate parameters determined. Given sufficient number of points, it appears that the initial concentration as well as the rate constant are predicted as global properties based taking limits as $t \longrightarrow 0$ of the polynomial expansion.It should be noted that the examples chosen here was a first order one; the method is general and they pertain to any form of rate law where the gradients and differential form can be curve-fitted and optimized as in section (2.3.3).

ACKNOWLEDGMENTS

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Chemical reaction rate determination II. numerical PIPD integral method

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Summary. In this second sequel, the integrated rate law expression is the basis for a new method of projecting all its parameters to be determined as function of one primary varying parameter -in this case the rate constant- by utilizing the experimental data points to construct the functional dependency where this method is called the principle of induced parameter dependence (PIPD). Such a technique avoids problems associated with multiple minima and maxima because of the possibly large number of parameters. The method is applied to first and second order reactions based on published data where the results accord very well with standard treatments. The PIPD and its method could be a promising optimization technique for a large class of phenomena that have a large number of parameters that need to be determined without leading to "unphysical" and anomalous parameter values.

1 INTRODUCTION

The PIPD application is tested against the same first order reaction (i) as in sequel I involving the methanolysis of ionized phenyl salicylate with data derived from the literature [1, Table 7.1,p.381]
and a second order reaction (ii) the details being
(ii) the reaction between plutonium(VI) and iron(II) according to the data in [2, Table II p.1427] and [3, Table 2-4, p.25].

Reaction (i) may be written

$$PS^- + CH_3OH \xrightarrow{k_a} MS^- + PhOH \qquad (1)$$

where for the rate law is pseudo first-order expressed as

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Reaction (ii) was studied by Newton et al. [2, eqns. (8,9),p.1429] and may be written as

$$\mathrm{Pu(VI)} + 2\mathrm{Fe(II)} \xrightarrow{k_b} \mathrm{Pu(IV)} + 2\mathrm{Fe(III)} \tag{2}$$

whose rate $\dot{\xi}$ is given by $\dot{\xi} = k_0[\mathrm{PuO_2^{2+}}][\mathrm{Fe^{2+}}]$ where k_0 is relative to the constancy of other ions in solution such as $\mathrm{H^+}$. The equations are very different in form to the first-order expressions and serves to confirm the viability of the current method. We use their data [2, TABLE II,p.1427] to verify the principles presented here. Espenson had also used the same data as we have to derive the rate constant and other parameters [3, pp.25-26] and we refer to his values for the final concentration parameter and rate constant to check on the accuracy of our methodology.

2 PIPD introduction

Deterministic laws of nature arefor the simplest examples written in the form

$$Y_{law} = Y_{law}(\mathbf{P}, k, t) \tag{3}$$

linking the variable Y_{law} to the experimental series of measurements of physical variable t (which in this case involves time). The components of $\mathbf{P}$, $P_i(i = 1, 2, ...N_p)$ and k are parameters. Verification of a law of form (3) relies on an experimental dataset $\{(Y_{exp}(t_i),\, t_i), i = 1, 2, ...N)\}$. Several methods [4, 5, 6, 7, etc.] have been devised to determine the optimal $\mathbf{P}, k$ parameters, but these methods consider the $(\mathbf{P}, k)$ parameters as autonomous and independent (e.g. [5]) subjected to free and independent variation during the optimization process. On the other hand, if one considers the interplay between the experimental data and Y_{law} one can derive certain parameters like the final concentration terms (e.g. λ_∞ and Y_∞ in what follows in Sec.(4)) if k, the rate constant is known. To preserve the viewpoint of interdependency, we devise a scheme that relates $\mathbf{P}$ to k for all P_i via the set $\{Y_{exp}(t_i), t_i\}$, and optimize the fit over k-space only. i.e. there is induced a $P_i(k)$ dependency on k via the the experimental set $\{Y_{exp}(t_i), t_i\}$. The advantages of the present method is that the optimization is over $1\,D$ k space, leading to a unique determination of $\mathbf{P}$ with respect to k, whereas if all $\mathbf{P}$ are considered equally free, the optimization could lead to many different local solutions for each of the $\{P_i\}$, some of which would be considered erroneous on physical grounds. The rate constant is considered constant over all measurements, although this assumption is not strictly correct [8].

3 Outline of Method

Let N be the number of dataset pairs $\{Y_{exp}(t_i), t_i\}$, N_p the number of components of the $\mathbf{P}$ parameter, and N_s the number of singularities where the use of a particular dataset (Y_{exp}, t) leads to a singularity in the determination of $\bar{P}_i(k)$ as defined below and which must be excluded from being used in the determination of $\bar{P}_i(k)$. Then $(N_p+1) \leq (N - N_s)$ for the unique determination of $\{\mathbf{P}, k\}$. Define ${}^{N-N_s}C_{N_p} = N_c$ as the total number of combinations of the data-sets $\{Y_{exp}(t_i), t_i\}$ taken N_p at a time that does not lead to singularities in P_i. Write Y_{law} in the form

$$Y_{law}(t, k) = f(\mathbf{P}, t, k). \tag{4}$$

Map $f \longrightarrow Y_{th}(\bar{\mathbf{P}}, t, k)$ as follows

$$Y_{th}(t, k) = f(\bar{\mathbf{P}}, t, k) \tag{5}$$

where the term $\bar{\mathbf{P}}$ and its components is defined below and where k is a varying parameter. For any of the $(i_1, i_2, \ldots, i_{N_p})$ combinations where $i_j \equiv (Yexp(t_{i_j}), t_{i_j})$ is a particular dataset pair, it is in principle possible to solve for the components of $\bar{\mathbf{P}}$ in terms of k through the following simultaneous equations:

$$\begin{aligned} Y_{exp}(t_{i_1}) &= f(\mathbf{P}, t_{i_1}, k) \\ Y_{exp}(t_{i_2}) &= f(\mathbf{P}, t_{i_2}, k) \\ &\vdots \\ Y_{exp}(t_{i_{N_p}}) &= f(\mathbf{P}, t_{i_{N_p}}, k) \end{aligned} \tag{6}$$

For each P_i, there will be N_c different solutions, $P_i(k,1), P_i(k,2), \ldots P_i(k,N_c)$. Define an arithmetic mean for the components of $\bar{\mathbf{P}}$ where

$$\bar{P}_i(k) = \frac{1}{N_c} \sum_{i=1}^{N_c} P_i(k,j). \tag{7}$$

Each $P_i(k,j)$ is a function of k whose derivative are known either analytically or by numerical differentiation. To derive an optimized set, then for the least squares method, define

$$Q(k) = \sum_{i=1'}^{N'} (Yexp(t_i) - Y_{th}(k,t_i))^2. \tag{8}$$

Then for an optimized k, we have $Q'(k) = 0$. Defining

$$P_k(k) = \sum_{i=1'}^{N'} (Y_{exp}(t_i) - Y_{th}(k,t_i)).Y'_{th}(k,t_i) \tag{9}$$

the optimized solution of k corresponds to $P_k(k) = 0$. The most stable numerical solution is gotten by the bisection method where a solution is assured if the initial values of k yield opposite signs for $P_k(k)$. Since all $P_i(k)$ functions are known, their values may all be computed for one optimized k value of Q in (8). For a perfect fit of Y_{exp} with Y_{law}, $Q(k') = Q'(k') = 0 \Rightarrow \bar{P}_j \rightarrow P_j$ $(\forall j)$ and so in this sense we define the above algorithm as giving optimized values for all P_i parameters via the k determination. This method is illustrated for the determination of two parameters in chemical reaction rate studies, of 1^{st} and 2^{nd} order respectively using data from the published literature referred to above.

4 Applications in Chemical Kinetics

The first order reaction studied here is reaction (i) and the second order one is reaction (ii) both described above. For both these reactions, we plot the $P_k(k)$ function as in Fig.(1) to test whether the method does in fact yield a unique solution. It can be observed that in both cases, a unique solution exists for $P_k(k) = 0$, and the region about this value of P_k is indicated a line for each of the reaction orders. The graph proves that for these systems a unique solution exists; as to whether this is a reasonable solution can only be deduced by comparison to experimental determinations and the results from other standard techniques. The details of deriving the P_k function, very different in form for the two reaction orders, are given in what follows.

4.1 First order results

For this order, the change in time t for any material property $\lambda(t)$, which in this case is the Absorbance $A(t)$ (i.e. $A(t) \equiv \lambda(t)$is given by

$$\lambda(t) = \lambda_\infty - (\lambda_\infty - \lambda_0)\exp(-k_a t) \tag{10}$$

for a first order reaction where λ_0 refers to the measurable property value at time $t = 0$ and λ_∞ is the value at $t = \infty$ which is usually treated as a parameter to yield the best least squares fit even if its optimized value is less for monotonically increasing functions (for positive $\frac{d\lambda}{dt}$at all t) than an experimentally determined $\lambda(t)$ at time t. In Table 7.1 of [1] for instance, $A(t = 2160s) = 0.897 > A_{opt,\infty} = 0.882$ and this value of A_∞ is used to derive the best estimate of the rate constant as $16.5 \pm 0.1 \times 10^{-3}\text{sec}^{-1}$.
For this reaction, the P_i of (4) refers to λ_∞ so that $\mathbf{P} \equiv \lambda_\infty$ with $N_p = 1$ and $k \equiv k_a$. To determine the parameter λ_∞ as a function of k_a according to (8) based on the *entire* experimental $\{(\lambda_{exp}, t_i)\}$ data set we invert (10) and write

$$\lambda_\infty(k) = \frac{1}{N'}\sum_{i=1'}^{N'} \frac{(\lambda_{exp}(t_i) - \lambda_o \exp -kt_i)}{(1 - \exp -kt_i)} \tag{11}$$

where the summation is for all the values of the experimental dataset that does not lead to singularities, such as when $t_i = 0$, so that here $N_s = 1$. We define the non-optimized, continuously deformable theoretical curve λ_{th} where $\lambda_{th} \equiv Y_{th}(t, k)$ in (5) as

$$\lambda_{th}(t, k) = \lambda_\infty(k) - (\lambda_\infty(k) - \lambda_0)\exp(-k_a t) \tag{12}$$

With such a projection of the λ_∞ parameter P onto k, we seek the least square minimum of $Q_1(k)$, where $Q_1(k) \equiv Q$ of (8) for this first-order rate constant k in the form

$$Q_1(k) = \sum_{i=1}^{N}(\lambda_{exp}(t_i) - \lambda_{th}(t_i, k))^2 \tag{13}$$

where the summation is over all the experimental $(\lambda_{exp}(t_i), t_i)$ values. The resulting P_k function (9) for the first order reaction based on the published dataset is given in Fig.(1).The solution of the rate constant k corresponds to the zero value of the function, which exists for both orders. The $\mathbf{P}$ parameters (λ_∞ and Y_∞) are derived by back substitution into eqs. (11) and (15) respectively. The Newton-Raphson (NR) numerical procedure [9, p.362]was used to find the roots to P_k.For each dataset, there exists a value for λ_∞ and so the error expressed as a standard deviation may be computed. The tolerance in accuracy for the NR procedure was $1. \times 10^{-10}$.
We define the function deviation fd as the standard deviation of the experimental results with the best fit curve $fd = \sqrt{\frac{1}{N}\{\sum_{i=1}^{N}(\lambda_{exp}(t_i) - \lambda_{th}(t_i)^2\}}$ Our results are as follows:
$k_a = 1.62 \pm .09 \times 10^{-2}\text{s}^{-1}$; $\lambda_\infty = 0.88665 \pm .006$; and $fd = 3.697 \times 10^{-3}$.
The experimental estimates are :
$k_a = 1.65 \pm .01 \times 10^{-2}\text{s}^{-1}$; $\lambda_\infty = 0.882 \pm 0.0$; and $fd = 8.563 \times 10^{-3}$.
The experimental method involves adjusting the $A_\infty \equiv \lambda_\infty$ to minimize the fd function and hence no estimate of the error in A_∞ could be made. It is clear that our method has a lower fd value and is thus a better fit, and the parameter values can be considered to coincide with the experimental estimates within experimental error. Fig.(2(a))shows the close fit between the curve due to our optimization procedure and experiment. The slight variation between the two curves may well be due to experimental uncertainties.

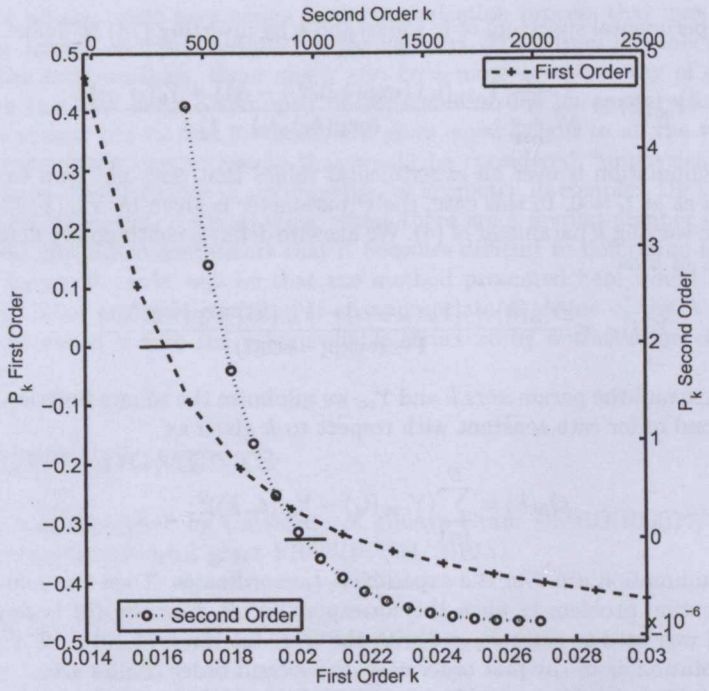


Fig. 1 P_k functions (9) for reactions (i) and (ii) of order one and two in reaction rate.

4.2 Second order results

To further test our method, we also analyze the second order reaction (2)

For Espenson, the above stoichiometry is kinetically equivalent to the reaction scheme [3, eqn. (2-36)]

$$PuO_2^{2+} + Fe_{aq}^{2+} \xrightarrow{k_b} PuO_2^{+} + Fe_{aq}^{3+}.$$

which also follows from the work of Newton et al. [2, eqns. (8,9),p.1429] whose data [2, TABLE II,p.1427] we use and analyze to verify the principles presented here. The overall absorbance in this case $Y(t)$ is given by [3, eqn(2-35)]

$$Y(t) = \frac{Y_\infty + \{Y_0\,(1-\alpha) - Y_\infty\}\exp(-k\Delta_0 t)}{1 - \alpha\exp(-k\Delta_0 t)} \tag{14}$$

where $\alpha = \frac{[A]_0}{[B]_0}$ is the ratio of initial concentrations where $[B]_0 > [A]_0$ and $[B] = [Pu(VI)]$, $[A] = [Fe(II)]$ and $[B]_0 = 4.47 \times 10^{-5}$M and $[A]_0 = 3.82 \times 10^{-5}$M . A rearrangement of (14) leads to the equivalent expression [3, eqn(2-34)]

$$\ln\left\{1 + \frac{\Delta_0\,(Y_0 - Y_\infty)}{[A]_0\,(Y_t - Y_\infty)}\right\} = \ln\frac{[B]_0}{[A]_0} + k\Delta_0 t. \tag{15}$$

According to Espenson, one cannot use this equivalent form [3, p.25] "because an experimental value of Y_∞ was not reported." However, according to Espenson, if Y_∞ is determined autonomously, then k the rate constant may be determined. Thus, central to all conventional methods is the autonomous and independent status of both k and Y_∞. We overcome this interpretation by defining Y_∞ as a function of

the total experimental spectrum of t_i values and k by inverting (14) to define $Y_\infty(k)$ where

$$Y_\infty(k) = \frac{1}{N'} \sum_{i=1'}^{N'} \frac{Y_{exp}(t_i)\{\exp(k\Delta_0 t_i) - \alpha)\} + Y_0(\alpha - 1)}{(\exp(k\Delta_0 t_i) - 1)} \tag{16}$$

where the summation is over all experimental values that does not lead to singularities such as at $t_i = 0$. In this case, the **P** parameter is given by $\mathrm{Y}_\infty(k) = P_1(k)$, $k_b = k$ is the varying k parameter of (4). We likewise define a continuously deforming function Y_{th} of k as

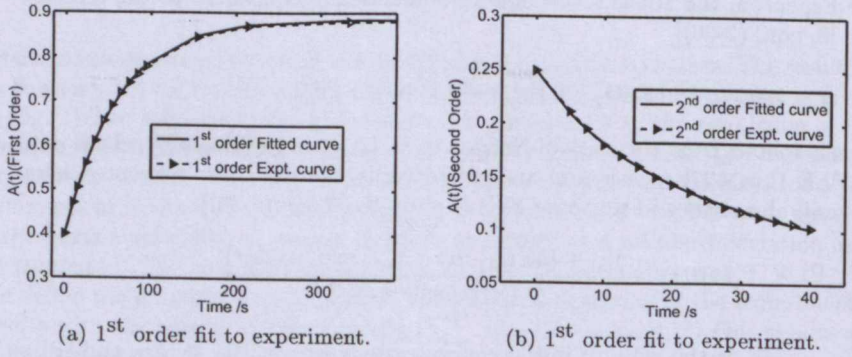
$$Y(t)_{th} = \frac{Y_\infty(k) + \{Y_0(1-\alpha) - Y_\infty(k)\}\exp(-k\Delta_0 t)}{1 - \alpha\exp(-k\Delta_0 t)} \tag{17}$$

In order to extract the parameters k and Y_∞ we minimize the square function $Q_2(k)$ for this second order rate constant with respect to k given as

$$Q_2(k) = \sum_{i=1}^{N} (Y_{exp}(t_i) - Y_{th}(t_i, k))^2 \tag{18}$$

where the summation are over the experiment t_i coordinates. Then the solution to the minimization problem is when the corresponding P_k function (9) is zero. The NR method was used to solve $P_k = 0$ with the error tolerance of 1.0×10^{-10}. With the same notation as in the first order case, the second order results are:
$k_b = 938.0 \pm 18\mathrm{M\ s}^{-1}$; $Y_\infty = 0.0245 \pm 0.003$; and $fd = 9.606 \times 10^{-4}$.

The experimental estimates are [3, p.25]:
$k_b = 949.0 \pm 22 \times 10^{-2}\mathrm{s}^{-1}$; $Y_\infty = 0.025 \pm 0.003$.
Again the two results are in close agreement. The graph of the experimental curve and the one that derives from our optimization method in given in Fig.(2).



(a) 1^{st} order fit to experiment. (b) 1^{st} order fit to experiment.

Fig. 2 Reaction (i) and (ii) results.

5 Conclusions

The results presented here show that by the method of inducing parameter dependency , it is possible to derive all the parameters associated with a theoretical curve by considering only one independent variable which serves as an independent

variable for all the other parameters in the optimization process that uses the experimental dataset as input variables in the calculus. Apart from possible reduced errors in the computations, there might also be a more accurate way of deriving parameters that are more determined by the value of one parameter (such as k here) than others; the current methods that gives equal weight to all the variables might in some cases lead to results that would be considered "unphysical". This might be so in the situations of optimization of geometry in complex DFT and ab initio quantum chemical computations, where there are a myriad number of possible mechanically stable conformers that it becomes difficult to determine the most prevalent forms. It could well be that the method presented here would indicate the average most probable structure if an appropriate analogue of the k variable is used that would induce the psot probable structure by optimization of the P_i parameters.

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